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Production of semiconductor quantum dots on polymer matrix by chemical method and their size control

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Abstract : Zero dimensional (0D) non-linear optical materials will have revolutionary implications in the future generation of optical information systems. As a source of 0D media quantum dots in the form of nanometer sized crystallites (nano crystals - Ncs) embedded in dielectric polymer matrices are found to be less expensive chemical routes over molecular beam epitaxy (MBE) methods. Of course, semiconductor clusters of few nanometers in size have attracted special attention because of their unique size dependent properties, which include optical and physico-chemical properties. Of all semiconductors, CdS has been used most frequently from a view point of the quantum size effect. In semiconductor quantum dots a continuous energy spectrum of electrons and holes inherent in a bulk crystal is reduced to a number of discrete levels. Accordingly, a set of absorption bands arises with the position controlled by the dot size. *A finite size distribution in real quantum dot ensembles as well as variations in potential barriers and defect concentrations in local environment, result in homogeneous broadening of the optical absorption and emission spectra.* In this realm, the present paper focuses on the chemical route of production of CdS quantum dots on polymer matrix and consequent control of crystallite sizes. The quantum dots thus prepared, are examined by X-ray diffraction and optical spectra studies. The consequent linking of the experimental observations to a theoretical model is also attempted in this paper. Our investigations have shown that diffusion treatment of hydrogen sulphide is much more reliable over direct treatment in controlling the size of the nano-crystallites.

Keywords : Nano-crystallites, semiconductor quantum dot, diffusion treatment

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1. Introduction

As a promising source of device application *e.g.* photonic switching, single electron transistor (SET) and other optical communication applications, optical studies of quantum dots have provided very interesting results. The physical effects are dominant in quasi zero-dimensional semiconductor nano-structures. High quality structures which are crowded with quantum dots for optical studies have become available by an number of different technologies. Apart from highly expensive and complex molecular beam epitaxy preparation technique, chemical routes also provide nano-crystallites as efficient as molecular beam epitaxy method. Semiconductor quantum dots in glass and polymer matrices have been the subject of many theoretical and experimental investigations [1-4]. Previously, several kind of thiols functional group like mercaptoethanol ($HOCH_2CH_2SH$), mercaptoethylamine ($H_3NCH_2CH_2SH$) *etc.* were found to act as additive elements to control the size of CdS nano particles [5]. The present paper outlines a brief theory and our recent efforts to prepare CdS quantum dots in new polymer films in view of relevant chemical methods of producing highly concentrated quantum dots of controlled sizes. The corresponding optical absorption and energy shift were studied by UV and Raman spectra respectively.

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2. Experimental

Aromatic solids like polyvinyl alcohol, being good solutes for water, were chosen as polymer matrices. In the aqueous (2%) solution of polyvinyl alcohol, cadmium chloride was added with varying concentrations (1,2,3 wt%) under a high stirring rate (200 rpm) condition. The constant temperature was maintained upto 70°C for 3 hours. The sample under preparation was kept whole night for complete dissolution to get a transparent solution. Again stirring condition was maintained at least upto 1 hour for the said temperature and kept undisturbed for slow

cooling process. To this solution, H_2S gas was passed directly upto its maximum absorbance. The CdS films were cast over glass substrates and allowed to dry in a closed chamber at room temperature and thus kept ready for subsequent experimentation. For another set, the films were cast at first then kept in an enclosed vessel and allowed to stay in semi-dry condition followed by H_2S diffusion reaction. The samples were kept undisturbed for 2-3 days for completion of the chemical reactions. The CdS films were now ready for successive experimentation.

In another technique, a mixture of styrene, acrylic acid (95:5), benzoyl peroxide (0.5% on monomer weight) and methanol were taken in a stoppered conical flask. The contents are then flushed with dry nitrogen gas. Polymerization of the co-polymer was carried out at the chosen temperature (65°C). After the completion of the experiment the films were cast using the same co-polymer. The films were dried in a vacuum oven at 40°C followed by neutralisation with ammonia and washed repeatedly with distilled water and dried in the same environment. The polymer was treated with $CdCl_2$ (1.5% approx.) solution overnight. It was further washed repeatedly with distilled water and dried. Finally, passivation and exposure to hydrogen sulphide gas yields nano-crystallites of CdS. All the parameters and conditions of preparation in the various steps have been optimized by trial and error.

3. Results and discussion

X-ray diffraction studies indicated that the CdS nanoparticles crystallized in the cubic β-phase in contrast to the bulk material (Figure 1). The average dimension of the crystallites as

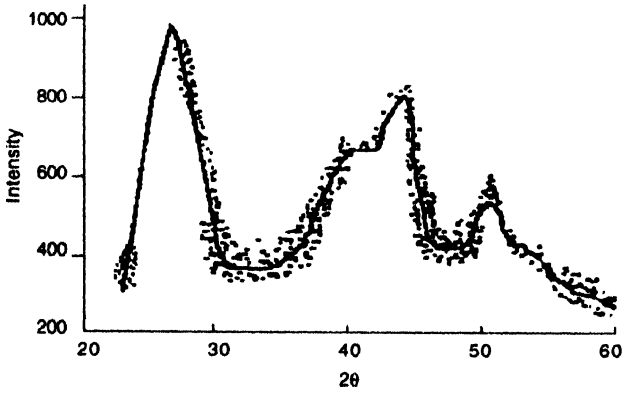

Figure 1. X-ray diffraction pattern of CdS in Polymer matrix

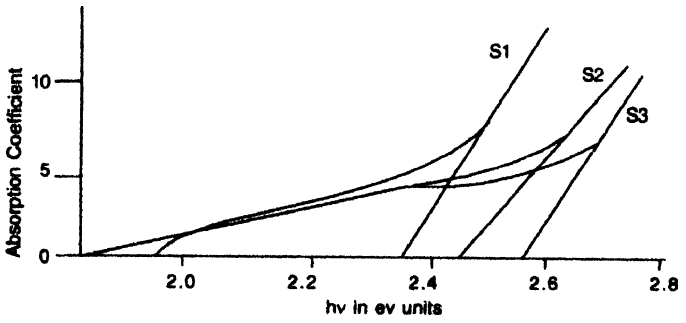

Figure 2. Absorption spectra of CdS in and near UV regime.

determined by Scherrer formula ($d = \lambda / W \cos\theta$, W being the full width at half maxima, θ the Bragg angle) are 8 nm, 2 nm, 1.5 nm respectively. The optical absorption spectra taken in the visible and near UV range show a considerable shift of the onset of absorption from the band edge of bulk CdS (Figure 2). The absorption edges exhibit the characteristic blue shift. This is a clear evidence of the shifts in the energy levels of the electrons and holes caused by the strong confinement in the quantum dots.

One can interpret the cause of blue shift with the help of a simple model. The semiconductor particles of high refractive index were supposed to be assembled in a medium of comparatively low refractive index (polymer matrix) so that the particles remove light from the incident light beam both by scattering and absorption. However, absorption dominates over scattering. Moreover, when the radius of the bound electrons in these semiconductor crystallites approach the Bohr excitonic radius (~ 5 nm); their electronic and optical properties start changing. This is the so-called quantum size effect [6]. In general, when the energy of the incident light is larger than the band gap, the electrons can be excited into conduction band leaving behind holes in the valence band. The energy levels of the electron or hole can be obtained for a spherical quantum dot of radius r, with infinite barrier at the dot polymer interface. These are given by

$$E^h_{n,l} = -\frac{0.0382}{(m_h / m_0)\, R^2}\, \alpha^2_{n,l},$$

for the hole and

$$E^e_{n,l} = \frac{0.0382}{(m_e / m_0)\, R^2}\, \alpha^2_{n,l} + E_g, \qquad (1)$$

for the electron.

The energy values as given above are expressed conveniently in units of eV with R in units of *nm* for quantum states characterized by the quantum numbers (n, l), $n = 1, 2, 3, 4$. and $l = 0, 1, 2, 3$ .... and $\alpha_{n,l}$ is the Spherical Bessel function of order unity ; m_h and m_e are effective band masses of the hole and electron respectively, m_0 is the free electron mass and E_g is the energy band gap of the semiconductor. Selection rules permit transitions satisfying $\delta n = 0$ and $\delta l = 0$. The blue shift spectral behaviour according to this model follows the $1/R^2$ behaviour. The absorption spectra here shows a blue shift with particle size (R) decreasing (samples S_1, S_2, S_3) and a large component of irregular broadening of the peaks found due to small cluster sizes (Figure 1).

Mie has formulated the theory of optical absorption for the small conducting spheres in the colloids [7]. In our case, we believe that the nano-crystallites as small conducting spheres positioned somewhere in the polymer matrix. The formulation could give a satisfactory description of the absorption behaviour

in the UV and near visible range. The reciprocal absorption length α satisfies the relation

$$\alpha h\nu = \text{const.}\,(h\nu - E_g)^n, \tag{2}$$

where n assumes the value 0.5 for a direct transition and 2 for an indirect one. As a consequence, the threshold excitation requires a contribution of lattice phonons in order to compensate for the change in the wave vector during the transition [8]. This theory is valid for extinction spectrum in the absence of quantum size effects. For CdS, the reciprocal absorption length near the band edge showed exponential dependence on photon energy as $\alpha = \exp(\beta h\nu / kT)$, β has a value 2.1 for single crystals [9]. Now one might think of independent scatterers as small and randomly oriented spheres, the mean separation of which is larger than the wave length of incident light and particle dimensions are much smaller than the incident light ($R << \lambda$). We define the complex dielectric constant as

$$\varepsilon = (n_p + ik_p)^2 = n_p^2 - k_p^2 + i(2k_p n_p), \tag{3}$$

where n_p and k_p are the refractive index of the particle and the absorption index which is proportional to the reciprocal absorption length α_p within the particle for light related with the wavelength, $k_p = \alpha_p \lambda / 4\pi$. The imaginary part of the dielectric constant is a direct measure of the light absorption by the particles. It increases steeply near the fundamental absorption edge.

The effects arising from the spatial confinement of charge carrier in semiconductors have also been the subject of intensive investigations [10, 11]. Earlier observations of confinement effects in these systems concerned small CdS particles in glass matrices [12, 13]. Quantum size effects are expected to occur when the Bohr radius of the first exciton in semiconductor becomes comparable with or larger than that of the particle. The Bohr radius r_B depends on the dielectric constant ε as per the relation

$$r_B = h^2 \varepsilon_0 \varepsilon / (e^2 \pi m^{eff}). \tag{4}$$

Considering ε as its real part, the contribution from eq. (3) in the case of CdS is found to be 8.9 and $m^{eff} = m_e^-$ yielding for the Bohr radius of the electron ~ 24 Å. Charge carrier confinements should become noticable when CdS particle radius decreases below this value.

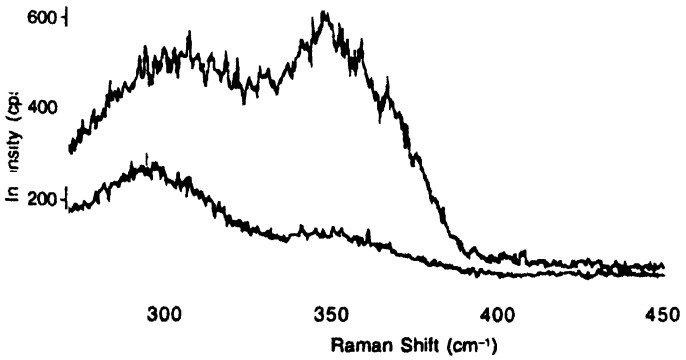

Figure 3. Raman spectra of CdS films prepared from 1:4 $CdCl_2$ and Polyvinyl alcohol for 1 and 3 wt% $CdCl_2$ solution for diffusion H_2S.

For the samples prepared by H_2S diffusion, it is found that for the stoichiometric ratio 1:4 of $CdCl_2$ and polyvinyl alcohol, the maximum shift (peak) is 295 cm^{-1} corresponding to normalised intensity ~ 300 cps; whereas for 1:15 ratio, the maximum peak is observed at 349 cm^{-1} for normalised beam intensity ~ 3200 cps. It clearly shows that the particle dimension being smaller, unable to scatter light at the low energy regime (Figures 3 and 4).

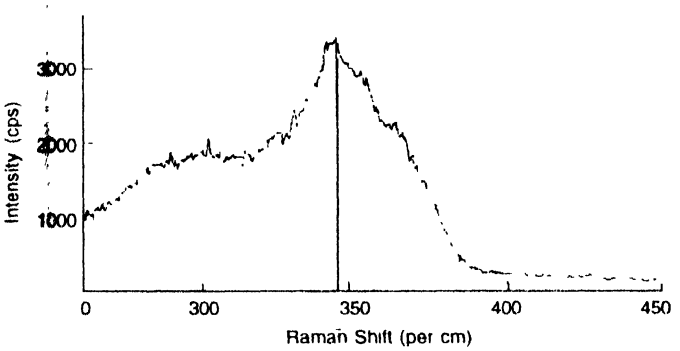

Figure 4. Raman spectra of CdS film prepared from 1:15 $CdCl_2$ and polyvinyl alcohol 1 wt% solution of $CdCl_2$ for diffusion H_2S

Again, there is a considerable shift of peak from 295 to 348 found for minor change in $CdCl_2$ concentration, claiming optimum value for controlled crystallites. However, for the samples prepared by direct H_2S treatment, there is no significant variation of peak which confirms that the diffusion treatment may have wide scope of controlling the dimension of the quantum dots assembled in the polymer host matrix compared to those prepared by direct treatment as assessed from Figure 5.

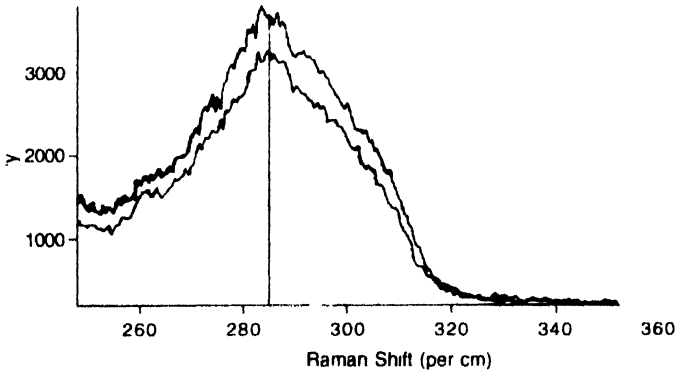

Figure 5. Raman spectra of CdS samples prepared from 1:4 $CdCl_2$ and Polyvinyl alcohol for 1 and 3 wt% $CdCl_2$ solution in direct H_2S treatment

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